

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
13 December 2001 (13.12.2001)

PCT

(10) International Publication Number
WO 01/93985 A1

- (51) International Patent Classification⁷: **B01D 53/04**
- (21) International Application Number: PCT/IN00/00060
- (22) International Filing Date: 7 June 2000 (07.06.2000)
- (25) Filing Language: English
- (26) Publication Language: English
- (71) Applicants (for all designated States except US):
GAS AUTHORITY OF INDIA LIMITED [IN/IN];
16, Bhikaji Cama Place, New Delhi 110 066 (IN).
CHEMISAR LABORATORIES [CA/CA]; 248, Silver-
creek Parkway N., Guelph, Ontario N1H 1E7 (CA).
- (72) Inventors; and
- (75) Inventors/Applicants (for US only): **RASTOGI,**
Ashutosh [IN/IN]; 16, Bhikaji Cama Place, R.K. Puram,
New Delhi 110 066 (IN). **CHUGH, Parivesh** [IN/IN];
16, Bhikaji Cama Place, R.K. Puram, New Delhi 110 066
(IN). **AHMED, Shamsuddin** [CA/CA]; 247 Cole Road,
Guelph, Ontario N1G 3K1 (CA). **PANDEY, Raj, Narain**
[CA/CA]; 34 Old Colony Trail, Guelph, Ontario N1G
4A9 (CA). **PANDEY, Rupesh, Narain** [CA/CA]; 34 Old
Colony Trail, Guelph, Ontario N1G 4A9 (CA).
- (74) Agent: **BHATNAGAR, Mahendra, Prasad;** Lall Lahiri
& Salhotra, N-128, Panchsheel Park, New Delhi 110 017
(IN).
- (81) Designated States (national): AE, AG, AL, AM, AT, AU,
AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE,
DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU,
ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS,
LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO,
NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR,
TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.
- (84) Designated States (regional): ARIPO patent (GH, GM,
KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian
patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European
patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE,
IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG,
CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).
- Published:**
— with international search report
- For two-letter codes and other abbreviations, refer to the "Guid-
ance Notes on Codes and Abbreviations" appearing at the begin-
ning of each regular issue of the PCT Gazette.



WO 01/93985 A1

(54) Title: PROCESS FOR STORAGE, TRANSMISSION & DISTRIBUTION OF GASEOUS FUEL

(57) Abstract: Storage of fuel gases, such as natural gas and its blends, at pressures of 400 to 600psig and ambient temperature, is achieved by containment within a container having an adsorbent material of microporous coconut shell carbon particles having been carbonized and partially oxidized to form monoliths of high packing density therein, and allowing the storage of about 130 to 160 liters of fuel per liter of adsorbent. The carbon monoliths are formed by grinding granular microporous carbon into a fine powder, mixing the powder with an aqueous dispersion of a binder material to form a slurry, heating the slurry until a moisture content of about 80 % to 100 % by weight is achieved, and consolidating the dried carbon-binder agent mixture at ambient temperature to obtain dense and mechanically strong carbon monoliths of regular shapes and desired dimensions.

**PROCESS FOR STORAGE , TRANSMISSION & DISTRIBUTION OF
GASEOUS FUEL**

FIELD OF THE INVENTION:

5 The present invention relates to a process for the safe storage, off-line transmission and distribution of gaseous fuels such as Natural Gas (NG) and Hythane stored at low pressure and ambient temperature and process for the preparation of adsorbent to be used in the purification unit and storage container.

10

The invention also resides in the process for the preparation of the adsorbents used in the purification unit for the storage of gaseous fuels, acting as guard bed to trap high hydrocarbon components of natural gas.

15 The embodiment of the present invention resides in the adsorbent and process for the preparation of such adsorbent prepared from granular microporous carbon preferably from the coconut shell to be used in the container containing fuel gases for the storage of such fuel gases at low pressure and ambient temperature.

20

Another embodiment of the invention resides in the thermal energy storage system comprising phase change materials to mitigate heat effects in the adsorption -desorption of natural gas.

25 The object of the invention is to prepare an adsorbent for storing and adsorbing the fuel gases at a low pressure of 400-600 psig at the ambient temperature resulting in the storage of the fuel as natural gas and its blends, in particular, Hythane, which is a mixture in the range of 5 -20% hydrogen and 80-95% natural gas by volume, of 150 litres of gas per litre of adsorbent.

30

Another object of the invention is to provide a method of binding together adsorbent particles comprising microporous carbon powders and granules in

order to yield compacted and mechanically strong monoliths of high packing density carbon to be utilized in storage container for efficient adsorptive storage and transportation of gaseous fuels such as natural gas and Hythane.

5 The invention specifically resides in storing the gaseous fuels at low pressures and the transportation and distribution of natural gas and blends of natural gas (particularly, Hythane fuel, which is a mixture in the range of 5 to 20 percent hydrogen and 80 to 95 percent natural gas by volume) for utilization of Natural Gas and/or Hythane, as fuel in applications such as
10 barbecue stoves, indoor cooking burners, automobiles and the like.

PRIOR ART

Presently, propane is used for outdoor and indoor domestic purposes as fuel in kitchen stoves, barbecue and the like purposes.

15

Further, the use of liquefied petroleum gas (LPG) consisting mainly of propane and butane for the domestic purposes is also widespread. Though LPG is convenient to store as it liquefies at moderate pressure and ambient temperature. However, LPG has several drawbacks as of potential fire
20 hazard. This is due to the fact that propane and butane vapours are heavier than air so that when spilled or leaked they will remain close to ground level thus creating a risk of fire or explosion. Moreover, LPG burning causes substantially larger emissions of CO₂ on the basis of per unit of energy generated.

25

The use of Natural gas for such purposes has also been tried because unlike that of propane, there is an abundant supply of natural gas with world reserves estimated to last more than 100 years. Since natural gas is lighter than air, it is inherently safe because upon accidental leakage it would rapidly
30 disperse. Natural gas also has the advantage of clean-burning characteristics with very low level emissions of toxic and regulated gases such as hydrocarbons, carbon monoxide and nitrogen oxides (NO and NO₂). Natural

gas is the least carbon intensive of the fossil fuels and therefore produces the least amount of carbon dioxide per unit of energy generated. The Octane rating of natural gas is about 130, substantially higher than octane rating of propane (105 - 110). The combination of an extensive resource base and
5 environmental advantages makes natural gas a preferred fuel.

For utilization of natural gas as fuel in cooking appliances, and Hythane as fuel in automobiles in places where pipeline transmission and distribution system of these gaseous fuels does not exist, it is required to provide an
10 alternative cost-effective and convenient means of storage, transportation and distribution of these gaseous fuels in these places.

Presently, natural gas is used mainly for fuelling stationery systems such as power plant combustors, industrial boilers, residential and commercial space
15 heaters and domestic appliances. In these applications , natural gas is supplied by gas pipe line technology. Its application in mobile systems is limited since the energy density of stored natural gas is low due to its gaseous nature. For the same reason, it has found little application as a domestic fuel in places where it is not available via pipelines.

20 Conventionally, the storage of natural gas is achieved by compression, liquefaction, dissolution, adsorption, clathration and encapsulation.

The most commonly perceived way is to store natural gas and its blends
25 under pressures between 3,000 to 5,000 psig. This method of high pressure storage requires use of very heavy and expensive storage cylinders and expensive fuelling equipment. The high pressure gas is also a safety hazard. In the case of an accident, high pressure natural gas and Hythane could explode due to ignition. Therefore, this method of high pressure Natural Gas
30 storage is not acceptable for use in barbecue stoves and indoor burners.

Another method of concentrating natural gas is to liquefy it at a temperature of -164°C . Natural gas is liquefied by a refrigeration cycle and stored in insulated tankers. The natural gas is reduced to about one six-hundredth of its original volume and the nonmethane components are largely eliminated.

5 This requires, however, that the liquefied natural gas be kept in insulated containers and stored under refrigeration conditions. This is also not found to be appropriate solution in the circumstances when the storage containers are taken to remote areas. Although liquefied natural gas contains two times more energy per unit volume than compressed natural gas at 2.49mpa, it is
10 not considered to be an economically viable solution due to the higher cost involved in refrigeration and liquefaction compared to its compression. Moreover, the refuelling procedures are more complex and hazardous for liquefied natural gas than for compressed natural gas.

15 Dissolution of natural gas in a liquid is another option of natural gas storage. The dissolved amount of natural gas is generally low, except when the solvent is ethane or propane. These solvents have, however, high volatiles and as the pressure in the container drops and the natural gas gets depleted, the concentration of ethane or propane increases in the gaseous phase,
20 which modifies the physical characteristics of the fuel mixture. However, this requires more complex and expensive ignition system. The part of solvents are lost and also in case of leak, the higher hydrocarbons tend to settle in low height areas instead of escaping to the atmosphere as is the case with natural gas, thus causing a fire or explosion hazard. Hence, the dissolution of
25 the natural gas in heavier hydrocarbons is also not a viable option.

The other option is to store natural gas by clathration and encapsulation. Clathrates are formed by inclusion of a guest molecule in a cavity made by several host molecules. The components are not held together by primary
30 valence forces, but the guest molecule is necessary for the stability of the host molecules structure. Natural gas hydrates are a kind of clathrate where methane molecules are held in water molecule cages. These natural gas

hydrates account for very large natural gas reserves in deep oceans and in the permafrost. The clathration of methane by either water or other compounds has been tried but methane storage is too low to be of any interest.

5

Further, encapsulation is another method for the storage of natural gas, which is quite similar to clathration, however, the same is also not found suitable as the storage capacity is low, refuelling requires very high pressure and the release mechanism for natural gas is also very complex.

10

To avoid such safety hazards, the solution founded is the use of adsorbents for storing such Natural Gas at low pressures. The adsorbents using monoliths of polyvinyl alcohol or other organic materials as binder are tried and found not to be sufficiently efficient for such adsorption.

15

The use of microporous materials such as zeolites, molecular sieves, and activated carbons have also been known for long for their adsorptive affinity of gases and vapours. The adsorption capacity of an adsorbent generally increases with its increasing internal surface area and pore volume.

20

However, with the activated carbon based adsorbent, it has generally been observed that higher the surface area, the lower is its packing density (that is, lesser weight of carbon can be packed into a fixed volume). This decrease of packing density is due partly to interparticle void spaces left while packing and partly due to intraparticle voidage arising from the development of macropores within the carbon network. Thus, although there is usually an increase in adsorption capacity on a weight basis of adsorbent with increase in the surface area, little or no gain is generally made in the adsorption capacity on a volume basis. However, for adsorptive storage of gaseous fuels such as natural gas and Hythane, the volume of the container holding the adsorbent is an important limiting factor. Unfortunately, the microporous carbons, which can be made only in the form of granules or powders from the precursor materials by methods known to the art have low packing density.

25

30

Thus, for applications of microporous carbons in the storage and transportation of natural gas and Hythane, it is necessary to consolidate them. The consolidation greatly reduces void spaces between carbon particles and possibly even macropore volume so that a larger quantity of adsorbent can be packed in a given storage volume. The compacted carbon so made is likely to exhibit higher adsorption capacity on the volume basis of adsorbent than is otherwise observed.

The presently known art of consolidating the carbon particles into shaped material for use in the storage of natural gas is based mainly on the use of organic binding materials which suffers from major disadvantages.

The polymer, polyvinylidene chloride (PVDC), which is often referred to by the Dow Chemical trade name Saran, has been used to bind KOH-activated coal carbon sold under trade name AX-21 to produce composite carbon pellets (Barton et al., Reports submitted to Ontario Ministry of Energy, 1984-85). This method has certain drawbacks. It requires the use of high percentages of polymer ranging from 30-90% by weight in the carbon-polymer mix. Furthermore, it is necessary to slowly heat the carbon-polymer composite pellets to a temperature of 700°C under vacuum in order to transform them into adsorbent. This heat treatment process liberates a large volume of corrosive HCl vapour, thus placing significant constraints on the materials of construction of the reactor. The heat treatment process can also generate vinyl chloride, a hazardous substance. Moreover, PVDC is not desirable to use as it is not a cost effective material and is also not easily available.

The use of phenolic resins for carbon binding and compaction of activated carbons made from coals and scrap tires into shaped material for use in storage of natural gas is also known to the art (see J. Sun, T.A. Brady, M.S. Rood, C.M. Lehmann, Energy and Fuels, Vol. II, pp 316-322, 1997). However, this class of binders also has a number of limitations. It is necessary to use large quantities of binder (binder to carbon ratio >0.3) and

to heat the carbon-binder mix to a high temperature ($>500^{\circ}\text{C}$) under compressive pressure to achieve binding. Furthermore, phenolic resins being condensation products of phenol and formaldehyde can potentially cause emissions of harmful substances, for example, formaldehyde, during the course of pressure-temperature moulding of the carbon-resin binder mix.

Another organic binder which has been used for compacting activated carbon powder derived from coal (sold under trade name AX-21) is polyvinyl alcohol (U.S. Patent No. 4,999,330). This method of binding using polyvinyl alcohol requires heating and cooling under carefully controlled conditions, is cumbersome and time-consuming.

Hence, the methods known in the art on fabrication of compacted carbon adsorbents for use in the storage of natural gas and other gaseous fuels are expensive, time-consuming, and are detrimental to health and the environment to quite an extent.

To overcome the drawbacks existing in the problems on compacting of microporous carbons for use in the storage of natural gas and to overcome the drawbacks associated with the techniques involved in the storage of natural gas, there is a need to use a high surface area material which can adsorb large quantities of natural gas at moderate pressures, where the natural gas molecules are adsorbed within the pores of a high surface area solid material using an adequate adsorbent. The subject invention has been evolved to overcome the above mentioned problems.

The adsorbent of this invention consists of carbon monoliths of high packing density fabricated by binding and compacting microporous carbon particles, prepared from coconut shells, using an inorganic clay material as binder.

30

In an another embodiment of the subject invention, the microporous carbon particles are prepared from the coal, coal coke, petroleum coke, wood and

rice husks and the like for the storage, transportation and distribution of natural gas and Hythane in accordance with this invention.

The use of non-toxic, non-hazardous, inexpensive and readily available
5 inorganic materials as binding agents for binding together carbon particles to form monoliths of desired shapes and sizes is achieved by using a cationic clay of phyllosilicate family, either alone or as a mixture with sodium silicate or calcium hydroxide, as the binding agent. Preferred cationic clay of the said binding agent formulation is bentonite, Na-exchanged bentonite or pillared
10 analogues of bentonite, preferably Al-, Fe-, Cr-, Zr- or Ti- pillared bentonite. In the said binder formulation, the clay content is 5% to 15% by weight, sodium silicate content is 0.5% to 1.5% by weight, and calcium hydroxide content is 0.5% to 1.5% by weight, all based on the weight of carbon in the monolith. The use of totally inorganic materials as binder in the subject
15 invention eliminates the risk of emission of toxic and regulated gases or vapour during monolith production.

The method of binding and compacting microporous carbon particles to yield high strength monoliths is achieved by mixing microporous carbon powder
20 with water dispersion of the cationic clay binding agent referred to above, drying the slurry to desired consistency, and consolidating the carbon-binder mix so prepared either by compression under a modest pressure in the range of 8,000 psi to 16,000 psi in a die/pelleting press without having to apply heating as done conventionally, or by the extrusion process using a
25 conventional extruder to yield dense, mechanically strong blocks of regular shape and desired dimension. The binding and compaction method, as disclosed above, causes nearly a two-fold reduction in bulk volume and a corresponding increase of packing density. As, the method does not require application of heat, it results in providing substantial processing cost savings.
30 Since, the method does not involve heating and cooling of the carbon-binder mix during monolith fabrication, the carbon-binder mix are formed into

monoliths in substantially little time as less as 15 minutes, thereby reducing the process time.

Moreover, the monolith fabrication process is not associated with release of obnoxious gases or vapours of any kind and therefore is free from environmental hazards or occupational health and safety concerns. The method thus overcomes the difficulties associated with the methods known to the art on pelletization or briquetting of activated carbon powders for using them in natural gas storage.

10

Accordingly, the subject invention relates to a process for storing the fuel gases such as natural gas and its blends in a container at a pressure of 400 psig to 600 psig at ambient temperature resulting in the storage of 130 litres to 160 litres of fuel per litre of adsorbent, comprising:

- 15 - feeding the said fuel gases or its blends from the source of supply to a compressor unit;
- passing the said compressed fuel gases through a pressure control and metering device to control the pressure of compressed natural gas at desired level;
- 20 - passing the said compressed pressure controlled fuel gases through a purification unit comprising adsorbent material preferably activated carbon prepared from coconut shells acting as guard bed to remove moisture, carbon dioxide and heavier hydrocarbons to get the purified fuel gases, and
- finally introducing the said purified gases in a storage container
- 25 containing adsorbent of microporous carbon particles prepared from coconut shells by means of carbonization and partial oxidation to form the monoliths of high packing density in a container.

The invention also relates to a process for the preparation of an adsorbent to be used in the guard bed of the said purification unit prepared from the coconut shell by the process comprising -

- cleaning the coconut shells of loose fibers and traces of kernel,

- crushing the said cleaned coconut shell to particle size of 8-12mm,
- washing the said crushed coconut shell with water
- drying the said washed coconut shell at a temperature of 370-385 K overnight
- 5 - loading the said dried coconut shells in a vessel purged with N₂
- mounting the said vessel containing said dried coconut shell vertically in a tube furnace and heating the same at a temperature of 870-880K for a period of two to four hours ;
- cooling the said vessel containing said dried coconut shell at room
- 10 temperature
- crushing and screening the said cooled coconut shell to obtain char having mesh size of 10-30 mesh fraction.
- treating the said crushed char with dilute Nitric acid at room temperature for four to six hours
- 15 - washing the said dilute nitric acid treated char in distilled water till char is free from acid;
- drying the said washed char at 375-385 K overnight.
- activation of said acid treated char by partial gasification with CO₂ under controlled conditions to obtain activated carbon to be used as guard
- 20 bed in the purification unit.

- The embodiment of the invention resides in an adsorbent prepared from granular microporous carbon preferably from the coconut shell to be used in the storage of fuel gases preferably natural gas and its blends at low pressure and ambient temperature , comprising the steps of:
- 25 a) grinding granular microporous carbon into a fine powder;
 - b) preparing an aqueous dispersion of a binder formulation by adding the ingredients of the said binder formulation to water and thoroughly stirring the mixture,
 - 30 c) mixing said powdered microporous carbon powder of step (a) with the said aqueous dispersion of the binding agent to make a carbon-binding agent-water slurry;

- d) drying the said carbon-binding agent-water slurry by evaporating water by heating while stirring until moisture content of the resultant mix corresponds to the range from 80% to 100% by weight, based on the weight of carbon in the mix;
- 5 e) consolidating the said dried carbon-binding agent mix at ambient temperature, to obtain dense and mechanically strong carbon monoliths of regular shapes and desired dimensions suited for the storage of gaseous fuels such as natural gas and Hythane; and
- 10 f) drying the said carbon monoliths at a temperature of 60° C to 70° C and at a temperature of 120°C to 140°C in air atmosphere to obtain moisture free dried carbon monoliths.

Another embodiment of the invention resides in a process for the preparation of a granular microporous carbon prepared by carbonization and controlled partial oxidation of coconut shells, comprising:-

- 15 - crushing the said coconut shells to a particle size of 5-10mm,
- washing the said crushed coconut shells with water and drying the same at a temperature of 110°C
- 20 - carbonizing the said washed and dried crushed coconut shells at a temperature of 600-700°C in an inert atmosphere to obtain the char,
- crushing and screening the said char to obtain the mesh size of 8-30,
- oxidizing the said crushed and screened char at a temperature of 700-850°C to obtain granular microporous carbon having surface area of 1200-1800m²/g
- 25

The said microporous carbon may also be derived from carbonaceous materials selected from wood, coal, various kinds of pitch, and petroleum tar.

30 The said granular microporous carbon is obtained by chemical activation in an inert atmosphere with KOH, phosphoric acid or ZnCl₂ at temperatures in the range 300-600°C or by carbonization at temperatures in the range 600-

800°C , followed by controlled partial oxidation with CO₂ or water vapour-N₂ mixture at temperatures in the range 700-850°C.

5 The consolidation of the said dried carbon-binding agent mix is obtained by compressing the said mixture, at ambient temperature, inside a suitable die at a pressure of 8,000 -16,000 psi using a suitable pelleting press or by extruding the said dried carbon-binding agent mix in a extruder .

10 The binding agent is selected from clay mixed with or without sodium silicate or calcium hydroxide .

The clay material is selected from the group consisting of cationic clays and pillared analogues of cationic clays selected from hydrous layer silicates of phyllosilicate family consisting of groups as smectite, vermiculite,
15 serpentine-kaolin, talc-pyrophyllite, mica, chlorite and sepiolite-palygorskite, typical examples being bentonite, atapulgite, hectorite, beidellite, fuller's earth halloysite, illite kaolin, montmorillonite and mullite.

20 The binding agent used is bentonite clay, Na- or K- exchanged bentonite clay, pillared bentonite clay (wherein pillaring species is a polycationic oxide of Al, Fe, Cr, Zr or Ti) and a combination thereof. The pillared analogues of cationic clays are materials in which small cations of the cationic clay are replaced by large polyoxocationic species.

25 The invention relates to a method for loading adsorbent material into a suitable storage container for adsorbing the fuel gas onto it at a pressure of about 400 to 600 psig and at ambient temperature (5-50°C), which results in storage of the fuel of about 150 litres of gas per litre of adsorbent.

30 The storage of this amount of natural gas in the same container without adsorbent is only possible at a very high pressure of about 2000 psi, which is unsafe and expensive for many applications. The adsorbent used are carbon

monoliths of high packing density fabricated by binding and compacting microporous carbon particles, prepared from coconut shells, using an inorganic clay material as binder. Natural gas or Hythane so stored in a suitable container can be transported and distributed by conventional or specially made carriers to any place, thus avoiding the need for pipeline system of distribution.

The present invention can better be understood with reference to the accompanying drawings, which are for illustrative purposes and should not in any way be construed to restrict the scope of the invention keeping in view that certain modifications and improvements are possible without deviating from the scope of the invention.

DETAILED DESCRIPTION OF THE ACCOMPANYING DRAWINGS

Figure 1 depicts the block flow diagram showing various unit operations involved in the preparation of high density monolithic microporous carbon adsorbent from coconut shells for use in the storage, off-line transportation and distribution of natural gas and Hythane fuels.

Figure 2 depicts the block diagram illustrating a process of storing of natural gas and Hythane with monolithic carbon adsorbent.

DETAILED DESCRIPTION OF THE INVENTION

As illustrated in Figure 1, microporous carbon for binding and consolidation in accordance with the process prepared from coconut shells by the two-stage process of carbonization and controlled partial oxidation. The raw coconut shells were crushed to particle size of 5-10 mm, washed with water and dried at a temperature of 110°C and then subjected to carbonization by heating to a temperature of 600°C to 700°C in an inert atmosphere. The char so produced was crushed, screened to 8-30 mesh size and then submitted to controlled partial oxidation with oxidising agents such as carbon dioxide and water vapour/nitrogen mixture at a temperature of about 700°C to about

850°C. The resultant product was a granular microporous carbon having a surface area in the range 1200 - 1800 m²/g. The source of microporous carbon suited for the storage of natural gas and Hythane is coconut shells. However, Microporous carbons derived from other sources such as coal, coal
5 coke, petroleum coke, wood and rice husks can also be used for storage, transportation and distribution of natural gas and Hythane.

The method comprises :

- (a) the crushing and milling the granular carbon into a fine powder by
10 conventional means preferably in a ball mill;
 - (b) preparing an aqueous dispersion of the binder formulation by adding the ingredients of the formulation to water (25 mL to 50 mL water per gram of binder) and thoroughly agitating the mix;
 - (c) mixing dry or pre-wetted carbon powder of step (a) with the water
15 dispersion of the binder of step (b) in appropriate proportions to make a slurry of carbon and binding agent;
 - (d) drying the carbon-binding agent slurry of step (c) to desired moisture content ranging from about 80% to about 100% by weight based on the weight of carbon used in step (c), by evaporating water while stirring in any
20 conventional blending-drying equipment;
 - (e) consolidating carbon-binder mix of step (d) either by compression, at ambient temperature, inside a suitable die under a pressure of 8,000 to 16,000 psi using a suitable pelleting press or by extrusion process using a suitable extruder to provide high density, mechanically strong monoliths of
25 desired shapes and sizes; and
 - (f) subjecting the monoliths to drying in steps at a temperature of 60°C to 70°C and at temperature of 120°C to 140°C in air atmosphere to provide dried monoliths free of moisture.
- 30 The said binding agent is a clay material used alone or as a mixture with sodium silicate or calcium hydroxide, wherein the clay component is chosen from a group of cationic clays which are hydrous layer silicates of the so-

called phyllosilicate family consisting of such groups as smectite, vermiculite, serpentine-kaolin, talc-pyrophyllite, mica, brittle mica, chlorite and sepiolite-palygorskite, typical examples being bentonite, atapulgite, hectorite, beidellite, fuller's earth, halloysite, illite kaolin, montmorillonite and mullite or from a group consisting of pillared analogues of cationic clays which are materials in which small cations of cationic clay are replaced by large polyoxocationic species. The most preferred clays for use in the binding agent formulation include bentonite clay, sodium exchanged bentonite clay, pillared analogues of bentonite clay (such as Al-, Fe-, Cr-, Zr- or Ti- pillared bentonite clay) and combinations thereof. In the said binding agent formulation, the clay content is about 5% to about 15% by weight, sodium silicate content is about 0.5% to about 1.5% by weight, and calcium hydroxide content is about 0.5% to about 1.5% by weight, all based on the weight of carbon used in step (c).

In step (d), the moisture content of the carbon-binder paste is controlled in the range from 80% to 100% by weight based on the weight of carbon used in the preparation.

The packing density of the monoliths so prepared is nearly twice as much as that of the starting granular material. The binding agents used in this invention are thermally and chemically stable substances which at no stages of monolith fabrication process release obnoxious gases or vapors of any kind and therefore there is no cause for concern from the viewpoint of environmental pollution or occupational health and safety hazard. Unlike prior art, the method of this invention does not require heating of carbon-binder during step (e) of the above-described embodiment, thereby making the process cost effective. Furthermore, since the method does not involve heating and cooling of the material during step (e) of the above-described embodiment, the said carbon-binder mix or paste can be processed to form monoliths in less than 15 minutes, thereby shortening the processing time.

Moreover, the subject process does not suffer from any drawback associated with the problem of pore plugging with binder because major ingredient of binder formulation (that is the clay component) is applied as a dispersion in water rather than as a solution wherein size of the clay particulates are too large to penetrate into and occupy the micropores of carbon particles. The method of binding and compaction of microporous carbon powder thus overcomes the difficulties associated with the prior art of pelletization or briquetting of activated carbon powders for use in the storage of natural gas.

10 The process for the storage of natural gas comprises packing the carbon monoliths prepared from coconut shell by the steps of carbonization and partial oxidation with steam or CO₂ activation binded together and consolidated into monoliths of high packing density in a storage container (1) of cylindrical or cuboidal geometry. The natural gas or its blends from the source (1) is fed via compressor (2) passes to flow control and metering device (4), via line (3), which is connected to pressure control and metering device (6) through pipe (5), which in turn is connected through a pipe (7) to a purification unit as a guard bed (8) packed with suitable solid adsorbent material, preferably activated carbon, carbon molecular sieve, zeolites or a combination thereof, which removes moisture, carbon dioxide and heavier hydrocarbons (C₄ and above) constituents present in small amounts in natural gas and Hythane. The exit stream from the purification unit (8) is then introduced via pipe line (9) into the adsorbent packed storage container (10) allowing adsorptive storage of Natural Gas under a pressure of 400 psig to 600 psig .

The present monolithic adsorbent produced from coconut shell microporous carbons by binding and compaction using the binding agents and method disclosed as above when packed in a container show high reversible uptakes of natural gas and Hythane on a volumetric basis, thus providing an efficient means of storage of natural gas and its blends. The method does not require expensive and heavy storage vessels, saves compression costs of high

pressure (3000 -5000 psig) storage, and offers safety because container pressure is limited to between 400 psig and 600 psig.

5 The adsorbent used in the guard bed are prepared from the coconut shell having a packing density of 0.5g/cm^2 and a surface area of about $1200\text{ m}^2/\text{g}$.

The process for the preparation of activated carbon from coconut shells for use as a guard bed is a two stage process :

- 10 1 pyrolysis/carbonization of dried coconut shell at 873 K under N_2 atmosphere.
- 2 Activation of coconut char by partial gasification/controlled oxidation with CO_2 at 1073K.

15 The coconut shells were cleaned of loose fibers and traces of kernel, crushed to particle size of 10mm, washed with water and dried at 383K overnight.

20 In a vessel, crushed and dried coconut shells are loaded , which is purged with inert gas, preferably N_2 : The vessel is mounted vertically in a tube furnace and heated at a temperature of 873K for a period of two to four hours and then allowed to cool at room temperature. The char so produced is crushed and screened to 10-30 mesh fraction.

25 The char thus produced is treated with dilute Nitric acid at room temperature for four to six hours. The dilute nitric acid treated char is then washed with distilled water till char is free from acid. The washed char is then dried at 383 K overnight.

30 The acid treated char is activated by partial gasification with CO_2 under well defined conditions. The activated carbon so obtained thus used as guard bed in the said purification unit.

The natural gas storage vessel can be filled with the natural gas under two conditions as slow filling and fast filling. When filling is done slowly heat liberated due to adsorption dissipates in the environment, while in case of fast filling, there is very little or no scope of heat dissipation to the environment.

5 As a result, adsorbent bed experiences a substantial rise in temperature. Since, adsorption of natural gas by the adsorbent decreases with increase of temperature, the temperature rise during fast filling causes a lowering of the gas stored by the adsorbent, similarly when the desorption is carried out rapidly, the temperature of the adsorbent bed drops substantially, affecting

10 the discharge of the stored gas.

The phase change materials may optionally be introduced in the storage vessel. These phase change materials absorb the heat liberated during the adsorption cycle by melting and then during the desorption cycle releases the

15 stored heat by freezing in the encapsulant and transfer the heat of fusion back to the adsorbent. The Phase change material thus increases the amount of natural gas that can be adsorbed during fast filling and also increases the amount of natural gas to be retrieved from the adsorbent during a rapid discharge cycle. The phase change material may be selected from the group

20 comprising C₂₀ Paraffin, C₁₈ Paraffin, C₁₇ Paraffin, C₁₅ Paraffin, CaCl₂.6H₂O

Storage containers can be filled in a central filling station and distributed therefrom. Thus, the transportation and distribution of natural gas and its blends by the method of this invention is not dependent upon an extensive

25 pipeline distribution infrastructure. Once a storage container becomes empty, due to, for example, usage of stored natural gas as fuel in kitchen stove, barbecue stove and like, it can be brought back to the filling station, refilled and transported back to the user. In this way the same batch of adsorbent placed in the storage container can be used for storage and

30 distribution of natural gas and/or its blends over and over again for years.

The subject invention can better be understood with reference to the undermentioned examples, which should not be construed to restrict the scope of the invention.

5 **EXAMPLES:**

EXAMPLE 1

Cylindrical shaped microporous carbon monoliths were fabricated by pressing carbon-binder mix contained in a cylindrical die by means of a hydraulic press
10 at pressures of 8,000 psi while maintaining the die at ambient temperature.

The carbon monoliths are prepared using microporous carbon obtained from coconut shells by first carbonizing the coconut shells by heating to a temperature at 600°C under inert atmosphere and then subjecting the char so
15 produced to controlled partial oxidation at 800°C using carbon dioxide as the oxidizing agent.

The binding agents used are bentonite clay mixed with sodium silicate. The said carbon-binder mix was prepared by thoroughly blending the fine powder
20 of microporous carbon with the binding agent formulation dispersed in water, and then partially drying the blend (slurry) by evaporation of water under vigorous stirring until the moisture content of the resultant carbon-binder mix corresponded to about 80% by weight based on the weight of dry carbon powder used in the preparation.

25 The binder dispersion was prepared by adding in the binder ingredients 25 mL water per gram of the binding agent and vigorously stirring the binder-water mixture.

30 The clay to carbon ratio in the said carbon mix binder is 0.10g/g, while the sodium silicate to carbon ratio in carbon-binder mix is 0.010g/g. The packing density of monolith was found to be 0.78 g/mL.

The monoliths were tested for the storage of natural gas fuel under a pressure of about 500 psig and at temperature of 22 °C. A batch of monoliths weighing 44.5 grams and having a total geometric volume 56.8 mL was used.

5

The natural gas storage capacity of the adsorbent was found to be 155 litres of natural gas per litre of adsorbent (155 v/v), as shown in Table 1.

TABLE 1:

10

Carbon Type	Binder Type	Binder Composition		Storage Capacity (v/v)
		Clay to carbon weight ratio	Calcium hydroxide to carbon weight ratio	
Coconut shell microporous carbon prepared by carbonization and partial oxidation with carbon dioxide; surface area = 1300 m ² /g	Bentonite clay and sodium silicate mixture	0.10	0.010	155

EXAMPLE :2

Cylindrical shaped microporous carbon monoliths were fabricated by pressing
5 carbon-binder mix contained in a cylindrical die by means of a hydraulic press
at pressures of 10,000 psi while maintaining the die at ambient temperature.

The carbon monoliths are prepared from coconut shells by first carbonizing
the coconut shells by heating to a temperature of 650°C under inert
10 atmosphere and then subjecting the char so produced to controlled partial
oxidation at 750°C using water vapour - N₂ mixture as oxidising agent.

The binding agents used were bentonite clay mixed with calcium hydroxide.
The said carbon-binder mix was prepared by the process as explained in
15 example 1.

The binder dispersion was prepared by adding in the binder ingredients 30
mL water per gram of the binding agent and vigorously stirring the binder-
water mixture.

20 The clay to carbon ratio in the said carbon mix binder is 0.10g/g, while the
calcium hydroxide to carbon ratio in carbon-binder mix is 0.010g/g. The
packing density of monolith was found to be 0.79 g/mL.

25 The monoliths were tested for the storage of natural gas fuel under a
pressure of about 500 psig and at temperature of 22 °C. A batch of monoliths
weighing 43.5 grams and having a total geometric volume 54.9 mL was used.

The natural gas storage capacity of the adsorbent was found to be 156 litres
30 of natural gas per litre of adsorbent (156 v/v), as shown in Table 2.

TABLE :2

Carbon Type	Binder Type	Binder Composition		Storage Capacity (v/v)
		Clay to carbon weight ratio	Calcium hydroxide to carbon weight ratio	
Coconut shell microporous carbon prepared by carbonization and partial oxidation with water vapour-N ₂ mixture; surface area = 1240 m ² /g	bentonite clay and calcium hydroxide mixture	0.10	0.010	156

5

EXAMPLE :3

Cylindrical shaped microporous carbon monoliths were fabricated by pressing carbon-binder mix contained in a cylindrical die by means of a hydraulic press
 10 at pressures of 12,000 psi while maintaining the die at ambient temperature.

The carbon monoliths are prepared from coconut shells by first carbonizing the coconut shells by heating to a temperature at 660°C under inert

atmosphere and then subjecting the char so produced to controlled partial oxidation at 720°C using water vapour - N₂ mixture as oxidising agent.

The binding agents used are Na-exchanged bentonite clay mixed with calcium hydroxide. The said carbon-binder mix was prepared by the process as explained in example 1.

The binder dispersion was prepared by adding in the binder ingredients 35 mL water per gram of the binding agent and vigorously stirring the binder-water mixture.

The clay to carbon ratio in the said carbon mix binder is 0.10g/g, while the ratio of calcium hydroxide to carbon in carbon-binder mix is 0.010g/g. The packing density of monolith was found to be 0.79 g/mL.

The monoliths were tested for the storage of natural gas fuel under a pressure of about 500 psig and at temperature of 22 °C. A batch of monoliths weighing 43.4 grams and having a total geometric volume 54.7 mL was used.

The natural gas storage capacity of the adsorbent was found to be 156 litres of natural gas per litre of adsorbent (156 v/v), as shown in Table 3.

TABLE: 3

Carbon Type	Binder Type	Binder Composition		Storage Capacity (v/v)
		Clay to carbon weight ratio	Calcium hydroxide to carbon weight ratio	

Coconut shell microporous carbon prepared by carbonization and partial oxidation with water vapour-N ₂ mixture; surface area = 1240 m ² /g	Na-exchanged bentonite clay and calcium hydroxide mixture	0.10	0.010	156
--	---	------	-------	-----

EXAMPLE 4

Cylindrical shaped microporous carbon monoliths were fabricated by pressing carbon-binder mix contained in a cylindrical die by means of a hydraulic press at pressures of 11,000 psi while maintaining the die at ambient temperature.

The carbon monoliths are prepared from coconut shells by first carbonizing the coconut shells by heating to a temperature at 670°C under inert atmosphere and then subjecting the char so produced to controlled partial oxidation at 735°C using water vapour - N₂ mixture as the oxidizing agent.

The binding agents used are Al-pillared bentonite clay mixed with sodium silicate.

The binder dispersion was prepared by adding in the binder ingredients 40 mL water per gram of the binding agent and vigorously stirring the binder-water mixture.

The clay to carbon ratio in the said carbon mix binder is 0.10g/g, while the sodium silicate to carbon ratio in carbon-binder mix is 0.010g/g. The packing density of monolith was found to be 0.78 g/mL.

- 5 The natural gas storage capacity of the adsorbent was found to be 156 litres of natural gas per litre of adsorbent (156 v/v), as shown in Table 4.

TABLE 4:

Carbon Type	Binder Type	Binder Composition		Storage Capacity (v/v)
		Clay to carbon weight ratio	Calcium hydroxide to carbon weight ratio	
Coconut shell microporous carbon prepared by carbonization and partial oxidation with water vapour-N ₂ mixture; surface area = 1240 m ² /g	Al-pillard bentonite clay and sodium silicate mixture	0.10	0.010	156

Cylindrical shaped microporous carbon monoliths were fabricated by pressing carbon-binder mix contained in a cylindrical die by means of a hydraulic press at pressures of 14,000 psi while maintaining the die at ambient temperature.

- 5 The carbon monoliths are prepared from coconut shells by first carbonizing the coconut shells by heating to a temperature at 665°C under inert atmosphere and then subjecting the char so produced to controlled partial oxidation at 755°C using water vapour - N₂ mixture as the oxidizing agent
- 10 The binding agents used are bentonite clay mixed with sodium silicate.

The binder dispersion was prepared by adding in the binder ingredients 42 mL water per gram of the binding agent and vigorously stirring the binder-water mixture.

15

The clay to carbon ratio in the said carbon mix binder is 0.10g/g, while the sodium silicate to carbon ratio in carbon-binder mix is 0.010g/g. The packing density of monolith was found to be 0.89 g/mL.

- 20 The monoliths were tested for the storage of natural gas under a pressure of about 500 psig and at temperature of 22 °C. A batch of monoliths weighing 48.0 grams and having a total geometric volume 53.7 mL was used.

- 25 The natural gas storage capacity of the adsorbent was found to be 156 litres of natural gas per litre of adsorbent (156 v/v), as shown in Table 5.

TABLE 5:

Carbon Type	Binder Type	Binder Composition	Storage Capacity (v/v)

		Clay to carbon weight ratio	Calcium hydroxide to carbon weight ratio	
Coconut shell microporous carbon prepared by carbonization and partial oxidation with water vapour- N ₂ mixture; surface area = 740 m ² /g	bentonite clay and sodium silicate mixture	0.10	0.010	156

EXAMPLE 6

Cylindrical shaped microporous carbon monoliths were fabricated by pressing
 5 carbon-binder mix contained in a cylindrical die by means of a hydraulic press
 at pressures of 16,000 psi while maintaining the die at ambient temperature.

The carbon monoliths are prepared from coconut shells as described in the
 foregoing examples.

10

The binding agents used were bentonite clay mixed with sodium silicate.

The binder dispersion was prepared by adding in the binder ingredients 50
 mL water per gram of the binding agent and vigorously stirring the binder-
 15 water mixture.

The clay to carbon ratio in the said carbon mix binder is 0.15g/g, while the sodium silicate to carbon ratio in carbon-binder mix is 0.015g/g. The packing density of monolith was found to be 0.67 g/mL.

- 5 The monoliths were tested for the storage of natural gas fuel under a pressure of about 500 psig and at temperature of 22 °C. A batch of monoliths weighing 36.6 grams and having a total geometric volume 54.9 mL was used.

- 10 The natural gas storage capacity of the adsorbent was found to be 154 litres of natural gas per litre of adsorbent (154 v/v), as shown in Table 6.

TABLE 6:

Carbon Type	Binder Type	Binder Composition		Storage Capacity (v/v)
		Clay to carbon weight ratio	Calcium hydroxide to carbon weight ratio	
Coconut shell microporous carbon prepared by carbonization and partial oxidation with water vapour-N ₂ mixture; surface area = 1750 m ² /g	Bentonite clay and sodium silicate mixture	0.15	0.015	154

In the examples 1-6 , the packing densities of the cylindrical shaped monoliths were ranging from 0.67-0.78, which was determined from their physically measured dimensions and weights. A batch consisting of 5 to 7 monoliths were used in the measurement. The weights were recorded after
 5 degassing the monoliths under vacuum at a temperature of about 130°C to about 150°C. The mechanical strength of the monoliths was tested in an apparatus consisting of a screw-thread type hand press attached to an electronic balance. Monolithic pieces were subjected to a constant compressive pressure of 5 kg/cm² (applied load divided by cross-sectional
 10 area of the monolith) and if found to remain intact it was concluded that the crushing strength of the particular monolith is at least 5 kg/cm². Packing density of the granular samples was measured by filling a calibrated cylinder with a known sample weight and tapping the cylinder until a constant volume was obtained. The surface area of granular carbon samples was determined
 15 from nitrogen adsorption isotherm measured at liquid nitrogen temperature using BET equation. The results are reported in **TABLE A**

oxidising agent	binder formula- tion	clay to Carbon ratio (g/g)	sodium silicate or calcium hydroxide to carbon ration (g/g)	packing density of granular carbon (g/mL)	packing density of monolith (g/mL)	mechanical strength (Kg/cm ²)
CO ₂	Bentonite clay - sodium silicate	0.10	0.010	0.45	0.78	> 5
H ₂ O vapour - N ₂ Mixture	Bentonite clay - calcium hydroxide	0.10	0.010	0.47	0.79	>5
H ₂ O	Na	0.10	0.010	0.47	0.79	>5

vapour - N ₂ Mixture	exchang ed Bentonite clay - calcium hydroxide					
H ₂ O vapour - N ₂ Mixture	Al- pillared Bentonite clay - sodium silicate	0.10	0.010	0.47	0.78	>5
H ₂ O vapour - N ₂ Mixture	Bentonite clay - sodium silicate	0.10	0.010	0.55	0.89	>5
H ₂ O vapour - N ₂ Mixture	Bentonite clay - sodium silicate	0.05	0.005	0.55	0.87	>5
H ₂ O vapour - N ₂ Mixture	Bentonite clay - sodium silicate	0.15	0.015	0.37	0.67	>5

The binding and consolidation with the bentonite clay based binding agents result in a increase in the packing density of the microporous carbons prepared by using different oxidizing agents and having different surface areas, thus making these materials suitable for the storage, transportation and distribution of gaseous fuels such as natural gas and Hythane, as illustrated in the Table A. The mechanical strength of the carbon monoliths

was found to be greater than 5 kg/cm² which is adequate for most applications.

EXAMPLE :7

5

The polyvinyl alcohol based binder was used for fabrication of carbon monoliths, where Carbon used was a mixture of two coconut shell carbons (surface area ~ 1100 m² and ~ 1600 m²/g) in the ratio 80 : 20. The binder was a mixture of 0.06 gram of polyvinyl alcohol (mol. wt. ~ 115,000), 0.004 gram of urea and 0.002 gram of ethylene glycol per gram of carbon. A slurry of carbon and binder ingredients in water was prepared, which was then partially evaporated to obtain a semi-dried mass with a moisture content of 40-50% by wt. (based on the total wt. of carbon used). Cylindrical shaped carbon monoliths of 20 mm diameter and 15-30 mm thickness were fabricated by pressing the semi-dried mass contained in a cylindrical die by means of a hydraulic press at a pressure of about 50,000 psi while slowly heating the die to a temperature of 250°C and holding at that temperature for about 1 hour. The average packing density of dried (moisture free) monoliths was 0.84 g/mL.

20

The monoliths were tested for the storage of natural gas fuel under a pressure of about 500 psig and at ambient temperature (22°C - 25°C). A batch of pellets weighing 44.7 grams and having a total geometric volume of 53.0 mL was used in the test. The natural gas storage capacity of the adsorbent was measured.

25

The natural gas storage capacity of the adsorbent was found to be 155 litres of gas per litre of adsorbent(155 v/v), as shown in Table 7.

TABLE :7

30

Natural Gas Storage by Monolithic Microporous Coconut Carbon Monoliths fabricated using Polyvinyl Alcohol based Binder at 500 psig Pressure and Ambient Temperature

Carbon Type	Binder Type	Binder Composition		Storage Capacity (v/v)
		PVA to carbon weight ratio	Urea and EG to carbon weight ratio	
Physical mixture of two coconut shell microporous carbons in the ratio 80 : 20; Surface area of the two carbons is ~ 1100 m ² /g and 1600 m ² /g, respectively	Polyvinyl alcohol (PVA), mixed with urea and ethylene glycol (EG)	0.06	Urea ---- = 0.004 Carbon EG ---- = 0.002 Carbon	155

EXAMPLE 8

- 5 Microporous carbon particles, prepared from coconut shells by carbonization and partial oxidation with water vapour - N₂ mixture and having surface area of about 1240 m²/g, were binded together and consolidated into cylindrical monoliths using an admixture of bentonite clay and sodium silicate as binding agent in the amounts of 0.10 gram of bentonite clay and 0.010 gram of
- 10 sodium silicate per gram of carbon. The average density of carbon monoliths was 0.79 g/mL.

The monoliths were tested for the storage of Hythane fuel (composition : 90 volume percent natural gas and 10 volume percent hydrogen) under a pressure of about 550 psig and at ambient temperature 25°C. A batch of monoliths weighing 44.5 grams and having a total geometric volume 56.5 mL was used in the test. The fuel storage capacity of the adsorbent was measured.

The Hythane storage capacity of the adsorbent was found to be 154 litres of Hythane per litre of adsorbent (154 v/v), as shown in Table 8.

TABLE :8

Hythane Storage by Monolithic Microporous Coconut Carbon at 550 psig Pressure and Ambient Temperature.

Carbon Type	Binder Type	Binder Composition		Storage Capacity (v/v)
		Clay to carbon weight ratio	Sodium silicate to carbon weight ratio	
Coconut shell microporous carbon prepared by carbonization and partial oxidation with water vapour-N ₂ mixture; Surface area = 1240/g	Bentonite clay and sodium silicate admixture	0.10	0.010	154

Examples 1-6, which deal with the monolithic carbon adsorbent fabricated using clay-based binders according to the method of this invention, clearly illustrate that the concentrated storage of natural gas at low pressures can be achieved by the method and adsorbent materials of this invention, thus
5 avoiding the high pressures needed for storage as compressed gas (CNG) or cryogenic temperatures needed for storage as liquefied natural gas (LNG).

Example 7, deals with the monolithic carbon adsorbent monoliths fabricated using PVA-based binder. It is evident from the above mentioned table that
10 PVA-based procedure is not only time-consuming, cumbersome and energy intensive but does not offer any advantages also. The natural gas storage capacity of the adsorbent fabricated using clay-based binders according to this invention, is similar to that of the adsorbent fabricated using PVA-based binder. On the other hand, the clay-based fabrication method has a number
15 of advantages: it is simple and easy-to-practice ; fabrication process does not require costly heating ; and there is no risk of releasing obnoxious gases or vapours. Example 8 illustrates that the method and adsorbent material of this invention is also well suited for low pressure adsorptive storage of Hythane fuel.

20 The natural gas and Hythane stored in portable containers by the method and adsorbent materials of this invention can be safely transported and distributed by conventional transport system. Storage containers can be fuelled in a central filling station. Once the natural gas or Hythane stored in a container is
25 exhausted due to usage as fuel in the desired application, the container can be brought back to the filling station, refilled and transported back to the user. In this way, the same batch of adsorbent can be used for storage and distribution of natural gas or Hythane over and over again for years.

30 While the invention has been described and illustrated herein by references to various specific materials, procedures and examples, it is understood that the invention is not restricted to the particular materials and procedures selected

for that purpose. Numerous variations of such details can be employed, as will be appreciated by those skilled in the art without deviating from the scope of the invention.

WE CLAIM:

1 A process for storing the fuel gases such as natural gas and its blends
in a container at a pressure of 400 psig to 600 psig at ambient temperature
5 resulting in the storage of 130 litres to 160 litres of fuel per litre of adsorbent,
comprising:

- feeding the said fuel gases or its blends from the source of supply to a compressor unit;
- passing the said compressed fuel gases through a pressure control
10 and metering device to control the pressure of compressed natural gas at
desired level;
- passing the said compressed pressure controlled fuel gases through a purification unit comprising said adsorbent material preferably activated carbon prepared from coconut shell acting as guard bed to remove moisture,
15 carbon dioxide and heavier hydrocarbons to get the purified fuel gases, and
- finally introducing the said purified gases in a storage container containing said adsorbent of microporous carbon particles prepared from coconut shells by means of carbonization and partial oxidation to form the monoliths of high packing density in a container.

20

2 A process as claimed in claim 1, wherein the phase change material may optionally be placed in the said container for the storage of said fuel gases along with said microporous carbon particles prepared from coconut shells.

25

3 A process as claimed in claim 1, wherein the said phase change material are selected from the group C₂₀ Paraffin, C₁₈ Paraffin, C₁₇ Paraffin, C₁₅ Paraffin, CaCl₂.6H₂O

30 4 A process as claimed in claim 1, for the preparation of an adsorbent to be used in the guard bed of the purification unit, prepared from the coconut shell by the process comprising -

- cleaning the coconut shells of loose fibers and traces of kernel,
- crushing the said cleaned coconut shell to particle size of 8-12mm,
- washing the said crushed coconut shell with water
- drying the said washed coconut shell at a temperature of 370-385 K
5 overnight
- loading the said dried coconut shells in a vessel purged with N₂
- mounting the said vessel containing said dried coconut shell vertically
in a tube furnace and heating the same at a temperature of 870-880K
for a period of two to four hours ;
- 10 - cooling the said vessel containing said dried coconut shell at room
temperature
- crushing and screening the said cooled coconut shell to obtain char
having mesh size of 10-30 mesh fraction.
- treating the said crushed char with dilute Nitric acid at room
15 temperature for four to six hours
- washing the said dilute nitric acid treated char with distilled water till
char is free from acid;
- drying the said washed char at 375-385 K overnight.
- activation of said acid treated char by partial gasification with CO₂
20 under controlled conditions to obtain activated carbon to be used in the
said guard bed in the purification unit.
- 5 An adsorbent prepared from the process as claimed in claim 4, to be
used in the said guard bed of the said purification unit.
- 25
- 6 A process as claimed in claim 1, wherein the said adsorbent prepared
from granular microporous carbon preferably from the coconut shell to
be used in the container for the storage of fuel gases preferably natural
gas and its blends at low pressure and ambient temperature ,
30 comprising the steps of:
a) grinding granular microporous carbon into a fine powder;

- b) preparing an aqueous dispersion of a binder formulation by adding the ingredients of the said binder formulation to water and thoroughly stirring the mixture,
- c) mixing said powdered microporous carbon powder of step (a) with the said aqueous dispersion of the binding agent to make a carbon-binding agent-water slurry;
- d) drying the said carbon-binding agent-water slurry by evaporating water by heating while stirring until moisture content of the resultant mix corresponds to the range from 80% to 100% by weight, based on the weight of carbon in the mix;
- e) consolidating the said dried carbon-binding agent mix at ambient temperature, to obtain dense and mechanically strong carbon monoliths of regular shapes and desired dimensions suited for the storage of gaseous fuels such as natural gas and Hythane; and
- f) drying the said carbon monoliths at a temperature of 60° C to 70° C and at a temperature of 120°C to 140°C in air atmosphere to obtain moisture free dried carbon monoliths.
- 7 An adsorbent prepared from granular microporous carbon preferably from the coconut shell prepared from the process as claimed in claim 6, to be used in the storage of fuel gases preferably natural gas and its blends comprising monolithic microporous carbon adsorbent contained in a portable container with natural gas or Hythane under a pressure of about 400 psig to 600 psig at ambient temperature.
- 8 A process as claimed in claim 6, wherein said microporous carbon is derived from carbonaceous materials selected from coconut shell, wood, coal, various kinds of pitch, and petroleum tar.

- 9 A process as claimed in claim 6, wherein the said granular microporous carbon is obtained by chemical activation in an inert atmosphere with KOH, phosphoric acid or ZnCl_2 at temperatures in the range 300-600°C .
- 5
- 10 A process as claimed in claim 6, wherein the said granular microporous carbon is obtained by carbonization at temperatures in the range 600-800°C , followed by controlled partial oxidation with CO_2 or water vapour- N_2 mixture at temperatures in the range 700-850°C.
- 10
- 11 A process as claimed in claim 6, wherein the said consolidation of the said dried carbon-binding agent mix is obtained by compressing the said mixture, at ambient temperature, inside a suitable die at a pressure of 8,000 -16,000 psi using a suitable pelleting press.
- 15
- 12 A process as claimed in claim 11, wherein the said consolidation of the said dried carbon-binding agent mix is obtained by extrusion using a extruder.
- 20
- 13 A process as claimed in claim 6, wherein the said binding agent is selected from clay mixed with or without sodium silicate or calcium hydroxide .
- 25
- 14 A process as claimed in claim 6, wherein the said clay material is selected from the group consisting of cationic clays and pillared analogues of cationic clays
- 30
- 15 A process as claimed in claim 14, wherein the said cationic clays is selected from hydrous layer silicates of the phyllosilicate family consisting of groups as smectite, vermiculite, serpentine-kaolin, talc-pyrophyllite, mica, chlorite and sepiolite-palygorskite, typical examples

being bentonite, atapulgite, hectorite, beidellite, fuller's earth halloysite, illite kaolin, montmorillonite and mullite.

- 16 A process as claimed in claim 15, wherein the said binding agent is
5 bentonite clay, Na- or K- exchanged bentonite clay, pillared bentonite
clay (wherein pillaring species is a polycationic oxide of Al, Fe, Cr, Zr
or Ti) and a combination thereof.
- 17 A process as claimed in claim 16, wherein the said clay binding agent
10 for fabrication of monolithic microporous carbon adsorbent is chosen
from a group consisting of pillared analogues of cationic clays which
are materials in which small cations of the cationic clay are replaced by
large polyoxocationic species.
- 18 A process as claimed in claim 16, wherein the said pillared clay binding
15 agent is a pillared bentonite clay where the said pillaring species is a
polycationic oxide of Al, Fe, Cr, Zr or Ti.
- 19 A process as claimed in claims 13 & 14, wherein the said binding
20 agent formulation is a mixture of bentonite clay and sodium silicate.
- 20 A process as claimed in claim 19, wherein the said binding agent
formulation is a mixture having 5% to 15% bentonite content by weight
and 0.5% to 1.5% sodium silicate content by weight, both based on the
25 weight of the carbon.
- 21 A process as claimed in claims 13 & 14, wherein the said binding
agent formulation is a mixture of bentonite clay and calcium hydroxide.
- 22 A process as claimed in claim 21, wherein the said binding agent
30 formulation is a mixture of 5% to 15% bentonite clay by weight and

0.5% to 1.5% calcium hydroxide by weight, both based on the weight of the carbon.

23 A process as claimed in claims 13 & 14, wherein the said binding
5 agent formulation is a mixture of Na-exchanged bentonite clay and calcium hydroxide.

24 A process as claimed in claim 23, wherein the said binding agent
10 formulation is a mixture of 5% to 15% Na- exchanged bentonite clay by weight and 0.5% to 1.5% calcium hydroxide by weight , both based on the weight of the carbon.

25 A process as claimed in claims 13 & 14, wherein the said binding
15 agent formulation is a mixture of Al-pillared bentonite clay and sodium silicate.

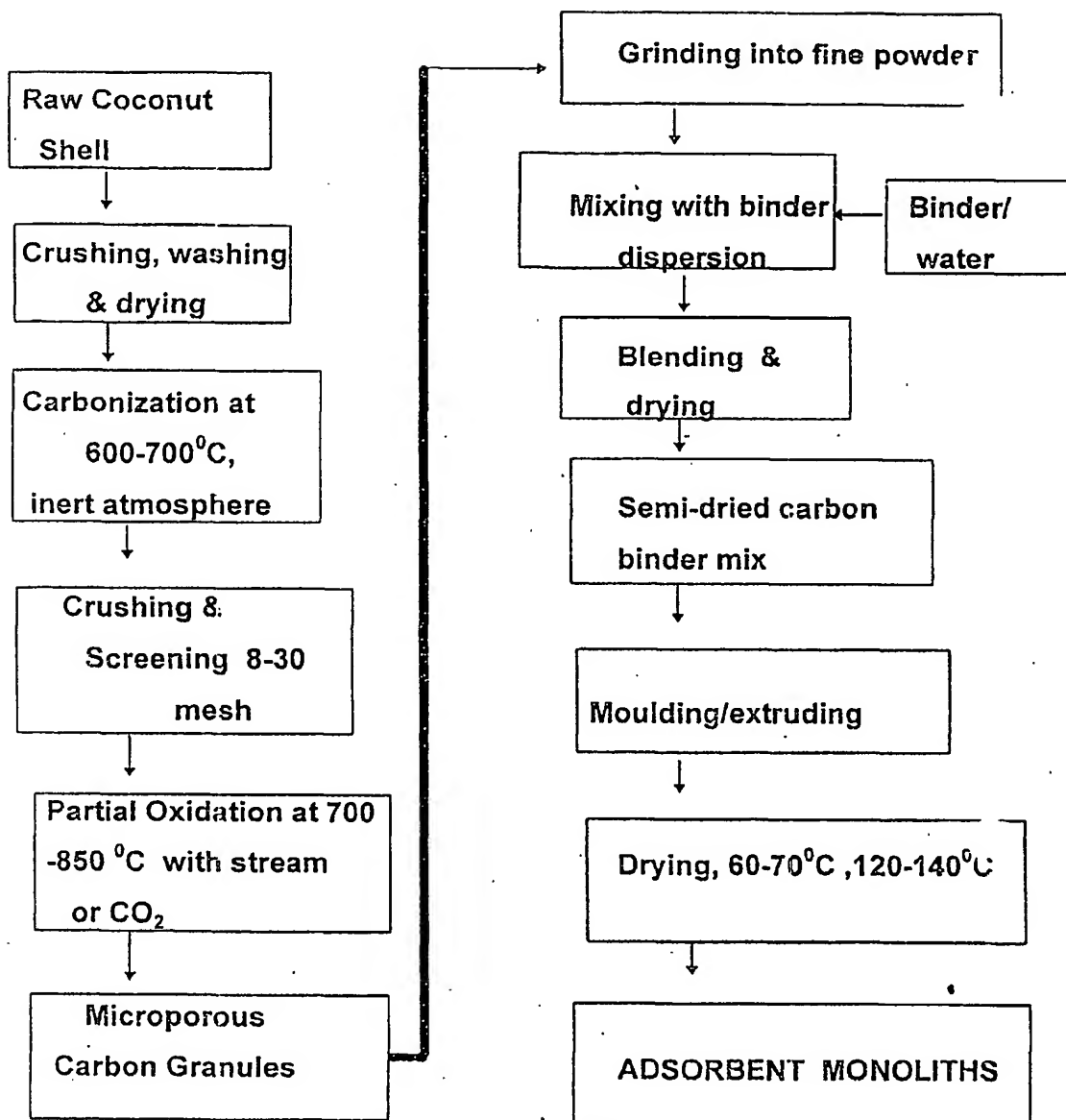
26 A process as claimed in claim 25, wherein the said binding agent
20 formulation is a mixture of 5% to 15% Al- pillared bentonite clay by weight and 0.5% to 1.5% sodium silicate by weight, both based on the weight of the carbon.

27 A process as claimed in any of preceding claims, wherein the said
25 binding agent as bentonite clay is used at a ratio of 0.05 - 0.15 gram of bentonite clay per gram of microporous carbon powder.

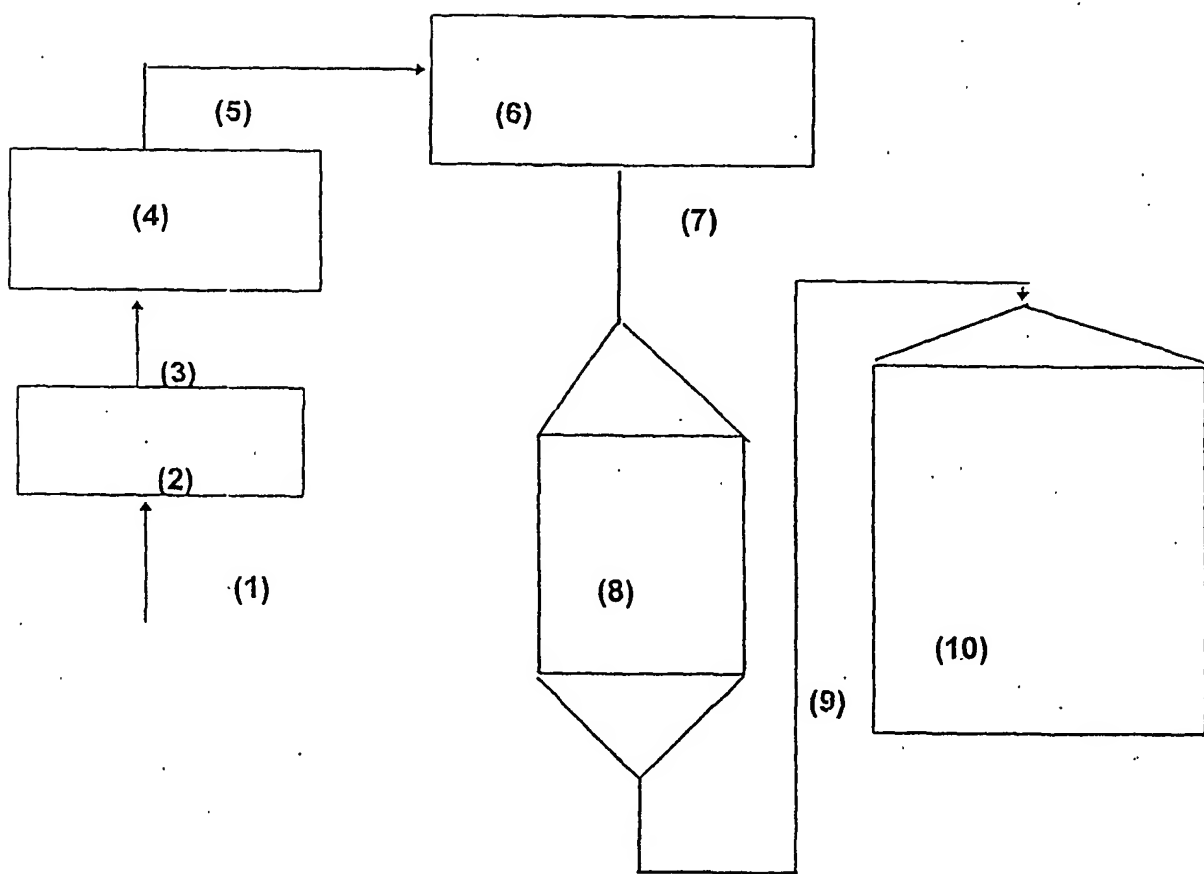
28 A process for the preparation of granular microporous carbon to be
used in the process as claimed in claim 6, prepared by carbonization and controlled partial oxidation of coconut shells, comprising:-

- crushing the said coconut shells to a particle size of 5-10mm,
- 30 - washing the said crushed coconut shells with water and drying the same at a temperature of 110⁰C

- carbonizing the said washed and dried crushed coconut shells at a temperature of 600-700⁰C in an inert atmosphere to obtain the char,
- crushing and screening the said char to obtain the mesh size of 8-30,
- oxidizing the said crushed and screened char at a temperature of 700-850⁰C to obtain granular microporous carbon having surface area of 1200-1800m²/g



2/2



INTERNATIONAL SEARCH REPORT

International application No.
PCT/IN00/00060

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) :B01D 53/04

US CL :95/143, 146; 96/143, 154; 502/437

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 95/95, 106, 114-115, 143-147, 901, 902; 96/108, 143-144, 146, 153-154; 502/416, 418, 428, 437

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
NONE

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
NONE

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4,580,404 A (PEZ et al.) 08 April 1986 (08.04.86).	1-28
A	US 4,749,384 A (NOWOBILSKI et al.) 07 June 1988 (07.06.88).	1-28
A	US 5,292,706 A (CHANG et al.) 08 March 1994 (08.03.94).	1-28
A	US 5,292,707 A (APARICIO et al.) 08 March 1994 (08.03.94).	1-28
A	US 5,324,703 A (MCCUE et al.) 28 June 1994 (28.06.94).	1-28
A	US 5,518,528 A (TOM et al.) 21 May 1996 (21.05.96).	1-28

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
A document defining the general state of the art which is not considered to be of particular relevance	*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
E earlier document published on or after the international filing date	*Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*Z* document member of the same patent family
O document referring to an oral disclosure, use, exhibition or other means	
P document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

09 JANUARY 2001

Date of mailing of the international search report

01 FEB 2001

Name and mailing address of the ISA/US
Commissioner of Patents and Trademarks
Box PCT
Washington, D.C. 20231

Facsimile No. (703) 305-3230

Authorized officer

ROBERT H. SPITZER

Telephone No. (703) 308-0651

INTERNATIONAL SEARCH REPORT

International application No.

PCT/IN00/00060

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5,639,707 A (LEWIS et al.) 17 June 1997 (17.06.97).	1-28
A	US 5,704,965 A (TOM et al.) 06 January 1998 (06.01.98).	1-28
A	US 5,710,092 A (BAKER) 20 January 1998 (20.01.98).	1-28
A	US 6,027,547 A (TOM et al.) 22 February 2000 (22.02.00).	1-28